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(54) **New monomers and oligomers containing a plurality of vinylbenzyl ether groups, method for their preparation and cured products therefrom.**

(57) Monomers and oligomers containing a plurality of vinylbenzyl ether groups are prepared by reacting a material containing a plurality of aromatic hydroxyl groups such as tetramethyltetrabromobisphenol A with a vinylbenzyl halide such as vinylbenzyl chloride in the presence of a polar aprotic solvent such as dimethylformamide. The monomers and oligomers prepared by this process have an improvement in one or more properties selected from dielectric constant (before and/or after moisture absorption) or thermal stability. Also disclosed are new monomers and oligomers containing a plurality of vinylbenzyl ether groups such as bis-(vinylbenzyl)ether of dicyclopentadienyl bisdimethylphenol.

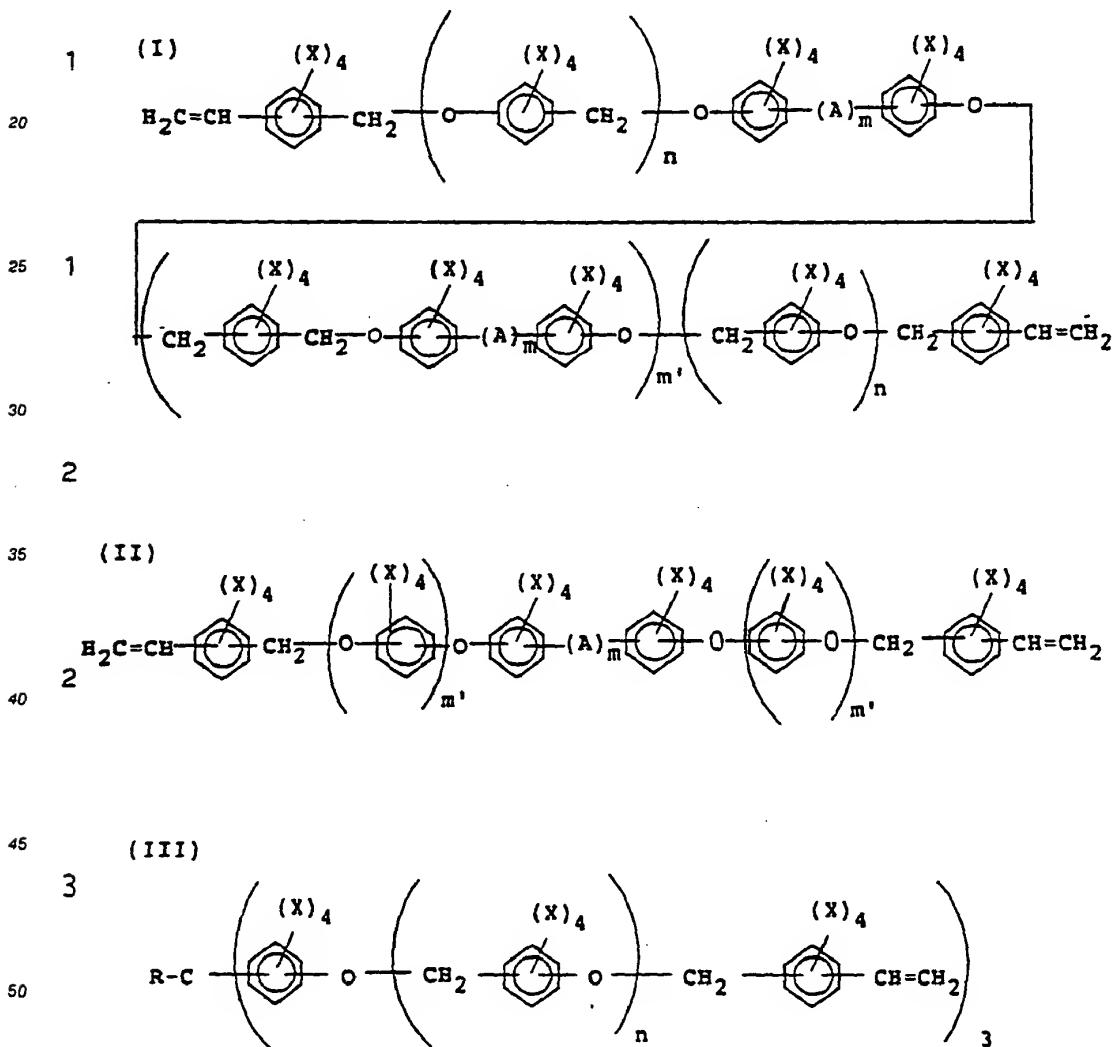
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NEW MONOMERS AND OLIGOMERS CONTAINING A PLURALITY OF VINYL BENZYL ETHER GROUPS, METHOD FOR THEIR PREPARATION AND CURED PRODUCTS THEREFROM

The present invention pertains to new compounds containing a plurality of vinylbenzyl groups and a method for their preparation.

Monomers having a plurality of vinylbenzyl ether groups have been prepared by Steiner in U.S. 4,116, 936 and Orlando et al in U.S. 4,170,711 by a process which comprises reacting a material having a plurality of aromatic hydroxyl groups with a vinylbenzyl halide in the presence of an alkali metal hydroxide and a solvent such as an alcohol. The monomers and oligomers prepared by this process have only a portion of the aromatic hydroxyl groups present converted to vinylbenzyl ether groups. It has been discovered that when the solvent employed is a polar aprotic solvent that more than 95% of the aromatic hydroxyl groups present converted to vinylbenzyl ether groups which results in an improvement in one or more of the properties selected from dielectric constant (before and/or after moisture absorption) or thermal stability. Also, the monomers and oligomers prepared by the process of the present invention do not need further purification such as by recrystallization as described in U.S. 4,116,936.

One aspect of the present invention pertains to monomers or oligomers containing a plurality of vinylaryl ether groups represented by the following formulas I-III



wherein A is a hydrocarbyl group having from 1 to 25, preferably from 1 to 15, most preferably from 1 to

about 10, carbon atoms, -O-, -S-, -S-S-,



5

O

"

-S-,

"

10

O



15 -C-; R is hydrogen or a hydrocarbyl group having from 1 to 12, preferably from 1-6, most preferably from 1 to 4, carbon atoms; each X is independently hydrogen, a hydrocarbyl or hydrocarbyloxy group having from 1 to 12, preferably from 1 - 6, most preferably from 1 to 4, carbon atoms or a halogen atom, preferably bromine; each m independently has a value of zero or 1; m' has a value of from zero to 200, preferably from zero to 50, most preferably from zero to 20 and each n independently has a value of zero or one; with the proviso that when m' and n have a value of zero then A is a dicyclopentadienyl group or a dicyclopentadienyl oligomer group.

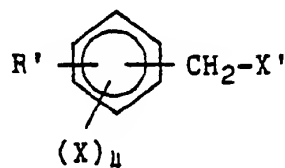
20 Still another aspect of the present invention pertains to a method for the preparation of cured compositions containing a plurality of vinylbenzyl ether groups which method comprises a 2-step heating cycle wherein the first step or gelation step is conducted at a temperature of from 60°C to 130°C, conducted at a temperature of from 175°C to 260°C.

25 Another aspect of the present invention pertains to a method for the preparation of materials containing a plurality of vinylbenzyl ether groups which comprises reacting at least one alkali metal phenoxide of a material containing a plurality of aromatic hydroxyl groups with a vinylbenzyl halide in the presence of a polar aprotic solvent and subsequently recovering therefrom a material wherein more than 95% of the aromatic hydroxyl groups have been converted to vinylbenzyl ether groups.

30 Another aspect of the present invention pertains to a method for the preparation of materials containing a plurality of vinylbenzyl ether groups which method comprises (A) reacting at least one alkali metal phenoxide of a material containing a plurality of aromatic hydroxyl groups with at least one chain extender material represented by the following formula IV

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(IV)



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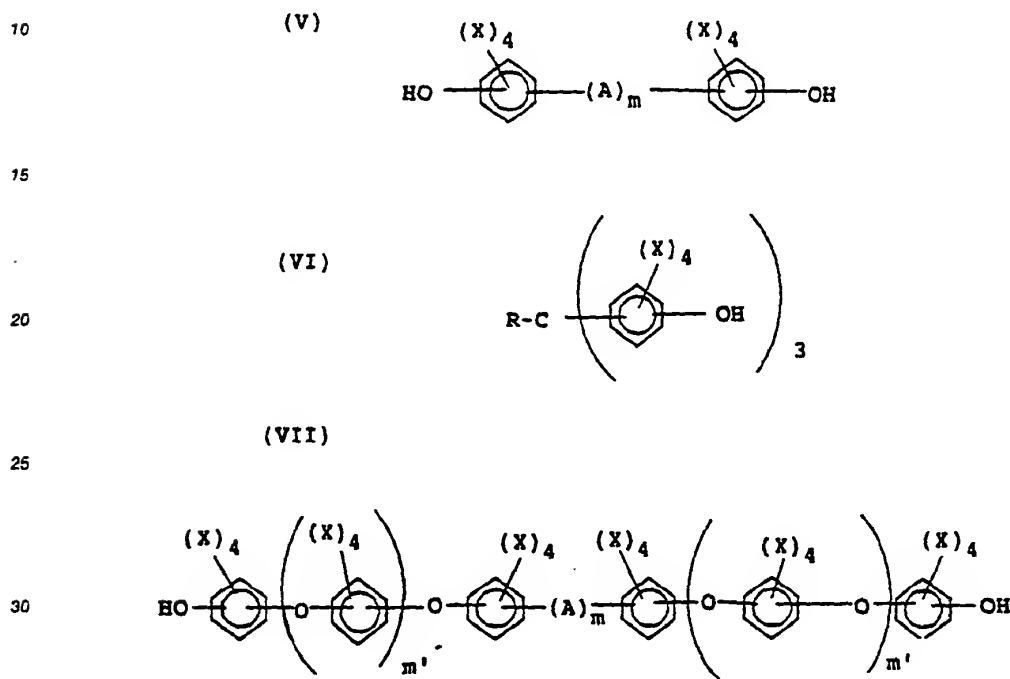
45 wherein R' is a hydroxyl group or a -CH₂X' group, X is as defined above and X' is a halogen, preferably chlorine or bromine in the presence of an alkali metal hydroxide and a polar aprotic solvent and then (B) reacting the alkali metal phenoxide of the resultant product with a vinylbenzyl halide in the presence of a polar aprotic solvent and subsequently recovering therefrom a material wherein more than 95% of the aromatic hydroxyl groups have been converted to vinylbenzyl ether groups.

50 Still another aspect of the present invention pertains to a method for the preparation of cured compositions containing a plurality of vinylbenzyl ether groups which method comprises a two-step heating cycle wherein the first step or gelation step is conducted at a temperature of from 60°C to 130°C, and the second step or curing step is conducted at a temperature of from 175°C to 260°C.

55 The term "hydrocarbyl" as employed herein includes, for example, alkyl, cycloalkyl, cycloalkadienyl and oligomers thereof, aryl, aralkyl, alkaryl, and alkenyl. Likewise, the term hydrocarbyloxy as employed herein includes, alkylloxy, cycloalkylloxy, aryloxy, aralkylloxy, alkarylloxy and alkenylloxy.

The reaction between the aromatic hydroxyl-containing materials and the vinylbenzyl halide materials or, when appropriate, the benzyl halide extender materials can be conducted at any suitable temperature which will substantially complete the reaction during the time employed. Suitable temperatures include those from -30°C to 100°C, preferably from 0°C to 80°C, most preferably from 15°C to 60°C. Suitable reaction time includes from 0.5 to 20, preferably from 0.5 to 15, most preferably from 0.5 to 6, hours.

Suitable hydroxyl-containing materials which can be employed herein include, for example, those represented by the following formulas V, VI and VII



wherein A, R, X, m and m' are as defined above. Particularly suitable aromatic hydroxyl-containing materials include, for example, dicyclopentadienylbis(2,6-dimethyl phenol), dicyclopentadienyl bis(ortho-cresol), dicyclopentadienyl bisphenol and combinations thereof. Such polycyclopentadienyl polyphenols and methods for their preparation can be found in U.S. Patent 4,390,680 issued to Donald L. Nelson. Also suitable hydroxyl-containing materials include, for example, resorcinol, bisphenol A, bisphenol F, bisphenol K, bisphenol sulfide, bisphenol sulfone, 3,3', 5,5'-tetramethyl bisphenol A, 3,3',5,5'-tetramethyl bisphenol F, 3,3',5,5'-tetramethyl bisphenol K, 3,3',5,5'-tetramethyl bisphenol sulfide, 3,3',5,5'-tetramethyl bisphenol sulfone, 3,3',5,5'-tetramethyl bisphenol 2,6-dibromo-3,3',5,5'-tetramethyl bisphenol F, 3,3',5,5'-tetramethyl-2,2',6,6'-tetrabromo bisphenol, 1,1,1-tri-(hydroxyphenyl)alkanes and combinations thereof. Suitable trihydroxyphenyl alkanes and method for their preparation can be found in U.S. Patent 4,394,496 issued to Paul G. Schrader.

Suitable vinylbenzyl halides which can be employed herein include, for example, vinylbenzyl chloride, vinylbenzyl bromide and combinations thereof.

Particularly suitable benzyl halide chain extenders which can be employed herein include, for example, 4-bromomethyl-3,5-dibromo-2,6-dimethyl phenol, 2,4-bis(chloromethyl)mesitylene, 4,6-bis(chloromethyl)-m-xylene, 2,5-bis(chloromethyl)-p-xylene, 1,2-bis(bromomethyl)benzene, 1,3-bis(bromomethyl)benzene, 1,4-bis(bromomethyl)benzene, 1,2-bis(chloromethyl)benzene, 1,3-bis(chloromethyl)benzene, 1,4-bis(chloromethyl)benzene and combinations thereof.

Suitable alkali metal hydroxides which can be employed herein include, for example, sodium hydroxide, potassium hydroxide, lithium hydroxide and combinations thereof.

Suitable polar aprotic solvents which can be employed herein include, for example, glycol ethers, ketones, cyclic ethers, nitriles, sulfones, phosphoramides and combinations thereof. Particularly suitable polar aprotic solvents include, for example, dimethylformamide, dimethylsulfoxide, dimethyl acetamide, N-methyl pyrrolidinone, dioxane, acetonitrile, tetrahydrofuran, ethylene glycol dimethyl ethers, 1,3-dimethoxy propane, 1,2-dimethoxy propane, tetramethylene sulfone, hexamethyl phosphoramide, methyl ethyl ketone, methyl isobutyl ketone, acetone and combinations thereof.

The vinylbenzyl ether-containing materials of the present invention are useful as coating materials, molding resins, particularly electrical molding resins, adhesives and in preparing laminates similar to those made from unsaturated polyesters. Cured products of bromine containing vinylbenzyl terminated monomers and oligomers have high glass transition temperatures (T_g), good thermal stability, low dielectric constant and excellent moisture-resistant properties and are therefore ideal flame retardant materials for use in preparing electrical laminates.

The resins disclosed herein can be combined with a variety of monomers containing unsaturated substituents such as, for example, styrene, α -methyl styrene, divinyl benzene, vinyl toluene, acrylate and methacrylate esters.

The vinylbenzyl ethers of polyphenols can also be blended with bismaleic anhydride imide, bismaleicimide, polypropargyl ethers of polyphenols, polycyanates, such as polyisocyanates of polyphenols, epoxy resins, liquid poly-1,2 or 1,4-butadiene, liquid epoxidized poly 1,2-butadiene, liquid butadiene-acrylonitrile copolymers and combinations thereof. Polyisocyanates of polyphenols include 1,3-dicyanato benzene; 1,4-dicyanato benzene; 1,3,5-tricyanato benzene; 4,4'-dicyanato bisphenol; 2,2-dicyanato-1,1'-binaphthyl; 2,2'-bis-4-cyanato phenyl propane; 4,4'-dicyanato bisphenyl sulfone; 4,4'-dicyanato bisphenyl sulfide; 4,4'-dicyanato-3,3',5,5'-tetramethyl diphenyl ether; 4,4'-dicyanato-3,3',5,5'-tetramethyl diphenyl propane; dicyclopentadienyl bis (4-cyanato benzene); dicyclopentadienyl bis (4-cyanato-3,5-dimethyl benzene) and mixtures thereof.

The vinylbenzyl ethers of polyphenols can also be blended with additive or modifier materials such as, for example, fillers, pigments, dyes, stabilizers, plasticizers, flexibilizers, surfactants, reinforcing materials, fire retardants, diluents and combinations thereof in conventional amounts.

The following examples are illustrative of the present invention but are not to be construed as to limiting the scope thereof in any manner.

EXAMPLE 1

To 1000 ml of a dimethylformamide (DMF) solution containing 282 g (0.75 mole) of dicyclopentadienyl-bis-(2,6-dimethyl phenol) in a reaction vessel equipped with a temperature control and indicating means, a means for stirring, cooling condenser and addition funnel was added 90 g (2.25 mole) sodium hydroxide at room temperature (25°C). The mixture was stirred under a nitrogen atmosphere for 4 hours at 40° to 45°C. The mixture turned dark green in color when the formation of the sodium phenoxides was completed. The solution was then cooled to 25°C and 275 g of vinylbenzyl chloride (1.8 mole of a 60/40 percent by weight mixture of the m-/p-isomers) was slowly added at 25° to 30°C over a period of 90 minutes. After completion of the addition, the mixture was maintained at a temperature of 35°C for 4 hours after which the solution turned blue in color. After maintaining the temperature at 45°C for 2 hours, the reaction mixture was cooled to room temperature and dry ice was added to neutralize any excess base. The DMF was removed by means of a rotating evaporator at 70°C to 80°C and a 10 mm Hg (1.33 MPa) vacuum. Then 1000 ml of a 27/75 percent by weight mixture of toluene/methyl ethyl ketone was added to the syrupy residue. The solution was washed with 120 to 200 ml of water several times until the pH of the material was 7. The organic layer was separated and concentrated under a 5 mm to 10 mm (0.67 to 1.33 MPa) vacuum at a temperature of from 60°C to 80°C. The 390 g of product obtained corresponded to a yield of 90% based on the dicyclopentadienyl-bis-(2,6-dimethyl phenol) without need for further purification. Infrared spectrum showed no residual phenolic hydroxyl groups remaining and chemical and ultraviolet (u.v.) analyses indicated that more than 99.9% conversion of the phenolic hydroxyl groups was achieved. The structure was confirmed by nuclear magnetic resonance (NMR) analysis to be the bis(vinylbenzyl) ethers of dicyclopentadienyl-bis-(2,6-dimethyl phenol).

Castings were made by heating the above prepared thermally reactive oligomers to a temperature of from 60°C to 80°C until completely melted, degassing at a temperature of less than 80°C under less than 5 mm Hg (0.67 MPa) vacuum to remove entrapped air and then pouring into a preheated (100°C) mold. The filled molds were heated at 120°C to 130°C for 1 hour, 170°C to 185°C for 2 hours and finally at 210°C to 220°C for 2 hours. The cured resin had a T_g of 210°C (by TMA) and 240°C (by DMA). The properties of the cured resin are given in Table I.

The samples were tested employing the following procedures.

10 THERMAL TESTS

Glass transition temperatures and other thermal data were determined by using a Dupont 943 Thermo Mechanical Analyzer (TMA) and a Dupont 982 Dynamic Mechanical Analyzer (DMA) with a Dupont 1090 Thermal Analyzer.

15 Thermogravimetric analysis was conducted on a Perkin-Elmer TGS-1 system. The samples (approximately 10 mg) were heated at 10°C/min. in a steady nitrogen stream of 35 cm³/min. The isothermal weight loss in air after 250 hours at 250°C was based upon the number obtained from a 1" x 2" x 1/8" (25.4 mm x 50.8 mm x 3.175 mm) coupon.

20

MOISTURE RESISTANCE

The weight gain due to moisture absorption was measured periodically at room temperature after immersing the clear castings into boiling water at 100°C. The weight gain is based upon the average number obtained from three 1" x 2" x 1/8" (25.4 mm x 50.8 mm x 3.175 mm) coupons. The water on the surfaces of the coupons was carefully wiped off prior to weighing.

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DIELECTRIC CONSTANT

The dielectric constants were obtained from 3" x 3" x 1/8" (76.2 mm x 76.2 mm x 3.175 mm) coupons measured with a Gen Rad 1689 bridge and a LD-3 cell.

35 COMPARATIVE EXPERIMENT A

The solvent disclosed in U.S. 4,116,936 was employed to prepare the product produced in Example 1. Thus, 94 g (0.25 mole) of dicyclopentadienyl-bis-o-cresol and 91.6 g (0.6 mole) of vinylbenzyl chloride, a 60/40 percent by weight mixture of the m-/p-isomers, were dissolved in 150 ml of acetone. The solution was heated to reflux and a solution of 49 g (0.75 mole) of potassium hydroxide (86%) in 100 ml of methanol was added over a period of 30 minutes. The mixture was refluxed for an additional hour. An additional 150 ml of acetone was added and the solution filtered to remove the precipitated potassium chloride. After adding 0.05 g of hydroquinone, the solution was evaporated to dryness on a rotating evaporator at 70°C under a 5 mm to 10 mm (0.67 to 1.33 MPa) vacuum. The viscous residual oil was worked up as described in Example 1 above. The resultant product was 119 g (76% yield based on dicyclopentadienyl bis-o-cresol) of bis-(vinylbenzyl)-ether of dicyclopentadienyl-bis-o-cresol with only 94% of the phenolic hydroxyl groups converted as determined by chemical and u.v. analysis. Infrared spectrum showed the broad absorption band of residual phenolic hydroxyl groups appearing at 3400 to 3500 cm⁻¹. The product was cured as in Example 1 and the results are given in Table I.

50

EXAMPLE 2

The same procedure of Example 1 was employed by reacting 270g (0.78 mole) of dicyclopentadienyl-bis(ortho-cresol) in 1000 ml DMF with 93 g (2.33 mole) of sodium hydroxide at 40°C for 4 hours. The same color change was observed when 286 g (1.87 mole) of vinylbenzyl chloride was added at 30°C. After work-up as in Example 1, 480 g of bis-vinylbenzyl ethers of dicyclopentadienyl-bis(o-cresol) was obtained which corresponded to a yield of 87% based on dicyclopentadienyl-bis(o-cresol) without further purification.

Infrared (IR) spectrum showed no residual phenolic hydroxyl groups remaining and chemical and u.v. analyses indicated that approximately 99.9% conversion of the phenolic hydroxyl groups was achieved. The structure was confirmed by NMR analysis as the bis(vinylbenzyl) ethers of dicyclopentadienyl-bis(o-cresol). The product was cured as in Example 1 and the results are reported in Table I.

TABLE I

Property	Example 1	Comp. Expt. A	Example 2
<u>BEFORE CURING</u>			
Gel Time @ 175°C, sec.	360-420	300-360	300-360
Exotherm			
Initial, °C	180	180	170
Maximum, °C	220	220	220
<u>AFTER CURING</u>			
Thermal Stability			
Temp. required to obtain 5% wt. loss, °C	415	355	395
Wt. loss after aging at 250°C for 250 hrs. in air, %	1.66	N.D. ³	2.60
Moisture pick-up after 200 hrs in boiling water at 100°C, %	0.3	N.D. ³	0.5
Dielectric Constant ¹ Frequency, dry/wet ²			
1000 Hz	2.713/2.860	2.863/3.009	2.820/N.D.
2000 Hz	2.711/2.854	2.861/3.007	2.816/N.D.
5000 Hz	2.709/2.851	2.859/3.004	2.812/N.D.
10000 Hz	2.705/2.849	2.857/3.001	2.807/N.D.
20000 Hz	2.697/2.837	2.855/2.999	2.797/N.D.
50000 Hz	2.699/2.838	2.851/2.994	2.798/N.D.
100000 Hz	2.686/2.827	2.848/2.988	2.784/N.D.
Dissipation Factor ¹ Frequency, dry/wet ²			
1000 Hz	.00167/.00217	.00149/.00170	.00265/N.D.
2000 Hz	.00167/.00212	.00150/.00183	.00259/N.D.
5000 Hz	.00165/.00217	.00161/.00205	.00267/N.D.
10000 Hz	.00176/.00240	.00180/.00241	.00273/N.D.
20000 Hz	.00196/.00277	.00206/.00302	.00284/N.D.
50000 Hz	.00248/.00370	.00262/.00425	.00310/N.D.
100000 Hz	.00289/.00460	.00313/.00552	.00343/N.D.

¹Dielectric constant and dissipation factor were measured at room temperature.

²This property was determined after 200 hours in 100°C boiling water.

³This property was not determined.

COMPARATIVE EXPERIMENT B

The solvent disclosed in U.S. 4,116,936 was employed to prepare the product produced in Example 2. Thus, 65g(0.187) mole of dicyclopentadienyl-bis-o-cresol and 71 g (0.467 mole) of vinylbenzyl chloride, a 60/40 percent by weight mixture of the m-/p-isomers, were dissolved in 200 ml of acetone. The solution was heated to reflux and a solution of 36 g of potassium hydroxide (86%) in 115 ml of methanol was added over a period of 30 minutes. The mixture was refluxed for an additional hour. An additional 200 ml of acetone was added and the solution filtered to remove the precipitated potassium chloride. After adding 0.05 g of hydroquinone, the solution was evaporated to dryness on a rotating evaporator at 70°C under a 5 mm to 10 mm Hg (0.67 to 1.33 MPa) vacuum. The viscous residual oil was worked up as described in Example 1 above. The resultant product was 80 g (77% yield based on dicyclopentadienyl bis-o-cresol) of bis-vinylbenzyl ether of dicyclopentadienyl bis-o-cresol with only 91% of the phenolic hydroxyl groups converted as determined by chemical and u.v. analysis.

EXAMPLE 3

A mixture containing 30 parts of divinyl benzene and 70 parts by weight of the divinylbenzyl ethers of dicyclopentadienyl bis(2,6-dimethyl phenol) prepared as in Example 1 was polymerized at 210°C to 220°C for 2 hours. The product was a tough clear resin. This product is designated as Sample 1. The dielectric constant and dissipation factor are given in Table II.

The product of Example 2 was copolymerized with divinyl benzene by heating to a temperature of from 60°C to 80°C until completely melted, degassing at less than 80°C under a less than 5 mm Hg. (0.67 MPa) vacuum to remove entrapped air and then pouring into a preheated (100°C) mold. The filled molds were heated at 120°C to 130°C for 1 hour, 170°C to 185°C for 2 hours and finally at 210°C to 220°C for 2 hours. This product is designated as Sample 2. The dielectric constant and dissipation factor are given in Table II.

TABLE II

	<u>Sample 1</u>	<u>Sample 2</u>
Dielectric Constant Frequency,		
1000 Hz	2.692	2.710
10000 Hz	2.683	2.701
100000 Hz	2.664	2.682
Dissipation Factor Frequency,		
1000 Hz	0.00192	0.00166
10000 Hz	0.00188	0.00184
100000 Hz	0.00241	0.00229

EXAMPLE 4

In a similar manner to Example 1, 51 g (0.2 mole) of methylene bis(2,6-dimethyl phenol) was reacted with 64 g (0.42 mole) of vinylbenzyl chloride in the presence of 18 g (0.44 mole) of sodium hydroxide and 150 g of di-methylformamide. There was obtained 72 g of viscous product. The structure was confirmed by NMR and IR analysis as being the bis(vinylbenzyl) ethers of methylene bis(2,6-dimethyl phenol). The oligomer was cured at 120°C to 130°C for 1 hour, 175°C for 1 hour, 200°C for 2 hours and finally at 230°C for 3 hours. The properties of the product before and after curing are given in Table III.

TABLE IIIBEFORE CURING

Gel Time @ 175°C, sec. 540

5 Exotherm

Initial, °C 180

Maximum °C 220-230

AFTER CURING

Thermal Stability Temp. required to obtain 5% wt. loss, °C 375

10 Wt. loss after aging at 250°C for 250 hrs. in air, % 3.44

Moisture pick-up after 100 hrs in boiling water at 100°C, % 0.4

EXAMPLE 5

15

The procedure of Example 1 was repeated except that 3,3',5,5'-tetramethyl-2,2',6,6'-tetrabromobisphenol (1), 3,3',5,5'-tetramethyl-2,2',6-tri-bromobisphenol (2), 3,3',5,5'-tetramethyl-2,6-dibromobisphenol F (3) were employed instead of the dicyclopentadienyl bis(2,6-dimethyl phenol). The corresponding products had no residual phenolic hydroxyl groups as determined by IR analysis. The products were cured as in Example 1 and their thermostabilities were compared with that of bis(vinylbenzyl) ethers of tetrabromobisphenol A as described in U.S. 4,116,936. Temperature required to obtain a 5% wt. loss and the weight loss after aging at 250°C for 250 hours in air are listed in Table IV.

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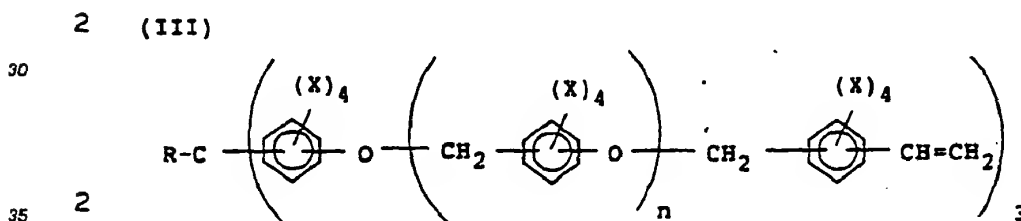
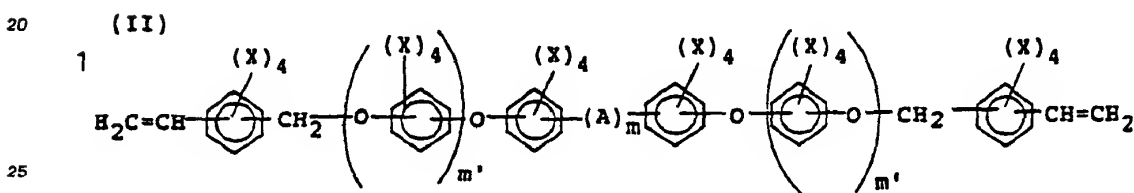
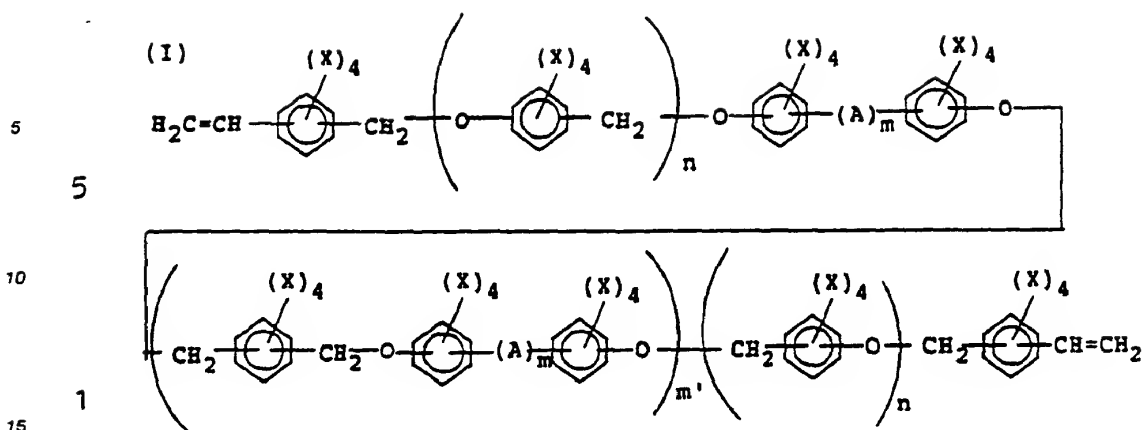
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TABLE IV
Thermal Stability of Bromine Containing Vinyl Benzyl-Terminated Monomers

Structure	Temperature at 5% weight loss in N ₂	Weight loss at 250°C			Dielectric Constant at 10 ³ Hz/R.T.	% wt. Gain through 200 hours in 100°C H ₂ O
		100 hours	150 hours	200 hours		
(1)	380°C	1.45	3.02	3.89	2.8	0.3
(2)	385°C	1.54	8.70	12.81	2.9	0.5
(3)	355°C	12.43	13.31	15.06	2.9	0.5
(4)	315°C	35.86	36.85	38.29	-	-

Claims

1. A monomer or oligomer containing a plurality of vinylaryl ether groups represented by the following formulas I, II, III



wherein A is a hydrocarbyl group having from 1 to 25 carbon atoms, -O-, -S-, -S-S-,



O

"

-S-,

"

O

or



R is hydrogen or a hydrocarbyl group having from 1 to 12 carbon atoms; each X is independently hydrogen, a hydrocarbyl or hydrocarbyloxy group having from 1 to 12 carbon atoms or a halogen atom; m' has a value of from zero to 200; each m and n independently has a value of zero or one; with the proviso that when m' and n have a value of zero, then A is a dicyclopentadienyl group or a dicyclopentadienyl oligomer group.

2. A monomer or oligomer as claimed in Claim 1 wherein A is a hydrocarbyl group having from 1 to 15 carbon atoms; R is hydrogen or a hydrocarbyl group having from 1 to 6 carbon atoms; each X is independently hydrogen, a hydrocarbyl or hydrocarbyloxy group having from 1 to 6 carbon atoms or a halogen atom; each m and n independently has a value of zero or 1; and m' has a value of from zero to 50.

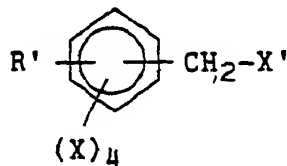
5 3. A monomer or oligomer as claimed in Claim 1 wherein A is a hydrocarbyl group having from 1 to 10 carbon atoms; R is hydrogen or a hydrocarbyl group having from 1 to 4 carbon atoms; each X is independently hydrogen, a hydrocarbyl or hydrocarbyloxy group having from 1 to 4 carbon atoms or a halogen atom; and m' has a value of from zero to 20.

4. A monomer or oligomer as claimed in Claim 1 wherein the monomer or oligomer is selected from the
10 group consisting of the bis(vinylbenzyl) ether of dicyclopentadienyl bis(2,6-dimethyl phenol), bis-(vinylbenzyl) ether of dicyclopentadienyl bis(o-cresol), bis(vinylbenzyl) ether of 3,3',5,5'-tetramethyl-2,2',6,6'-tetrabromobisphenol, bis (vinylbenzyl) ether of 2,6-dibromo-3,3',5,5'-tetramethyl bisphenol F and bis (vinylbenzyl) ethers of 3,3',5,5'-tetramethyl-2,2',6-tribromobisphenol.

5. A method for the preparation of materials containing a plurality of vinylbenzyl ether groups which
15 comprises reacting at least one alkali metal phenoxide of a material containing a plurality of aromatic hydroxyl groups with a vinylbenzyl halide in the presence of a polar aprotic solvent and subsequently recovering therefrom a material wherein more than 95% of the aromatic hydroxyl groups have been converted to vinylbenzyl ether groups.

6. A method for the preparation of materials containing a plurality of vinylbenzyl ether groups which
20 comprises (A) reacting at least one alkali metal phenoxide of a material containing a plurality of aromatic hydroxyl groups with at least one chain extender material represented by the following formula IV

(IV)

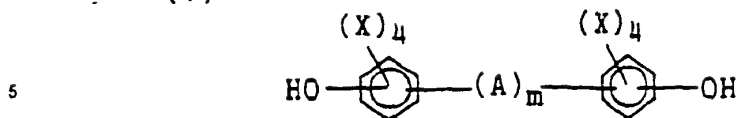


30 wherein R' is a hydroxyl group or a -CH₂X' group; each X is independently hydrogen, a hydrocarbyl or hydrocarbyloxy group having from 1 to 12 carbon atoms or a halogen atom; and X' is a halogen; in the presence of a polar aprotic solvent and then (B) reacting the alkali metal phenoxide of the resultant product with a vinylbenzyl halide in the presence of a polar aprotic solvent and subsequently recovering therefrom a material wherein more than 95% of the aromatic hydroxyl groups have been converted to vinylbenzyl ether
35 groups.

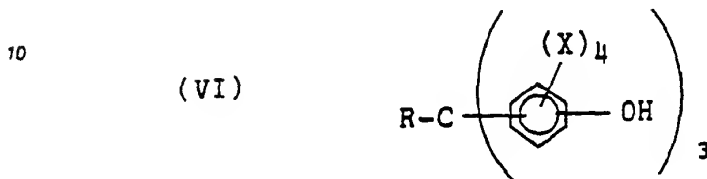
7. A method as claimed in Claim 5 or Claim 6 wherein

(a) said material containing a plurality of aromatic hydroxyl groups is a material represented by the following formulas V, VI or VII

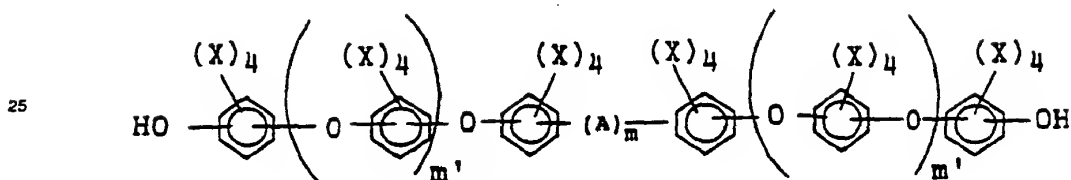
(V)



(VI)



(VII)



wherein A is a hydrocarbyl group having from 1 to 25 carbon atoms, -O-,

-S-, -S-S-,

$\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}- \end{array}$,

O

"

-S-,

"

O

or

$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$;

R is hydrogen or a hydrocarbyl group having from 1 to 12 carbon atoms; each X is independently hydrogen, a hydrocarbyl or hydrocarbyloxy group having from 1 to 12 carbon atoms or a halogen atom; each independently has a value of zero or 1; and m' has a value of from zero to 200;

(b) said extender material is 4-bromomethyl-3,5-dibromo-2,6-dimethyl phenol, 2,4-bis(chloromethyl)-mesitylene, 1,2-bis(bromomethyl)benzene, 1,3-bis(bromomethyl)benzene, 1,4-bis(bromo-methyl) benzene, 1,2-bis(chloromethyl)benzene, 1,3-bis(chloromethyl)benzene, 1,4-bis(chloromethyl)benzene, 4,6-bis(chloromethyl)-m-xylene, 2,5-bis(chloromethyl)-p-xylene, and combinations thereof;

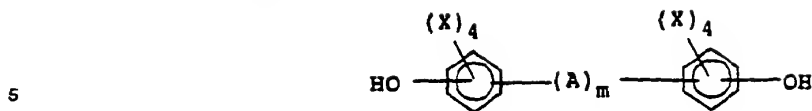
(c) said vinylbenzyl halide is vinylbenzyl chloride or vinylbenzyl bromide; and

(d) said polar aprotic solvent is dimethylformamide, dimethyl acetamide, dimethylsulfoxide, N-methyl pyrrolidinone, dioxane, acetonitrile, tetrahydrofuran, ethylene glycol dimethyl ether, 1,2-dimethoxy propane, tetramethylene sulfone, hexamethyl phosphoramide, methyl ethyl ketone, methyl isobutyl ketone, acetone or mixtures thereof.

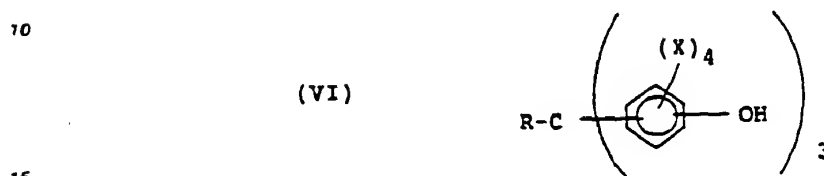
8. A method as claimed in Claim 5 or 6 wherein

(a) said material containing a plurality of aromatic hydroxyl groups is a material represented by the following formulas V, VI or VII

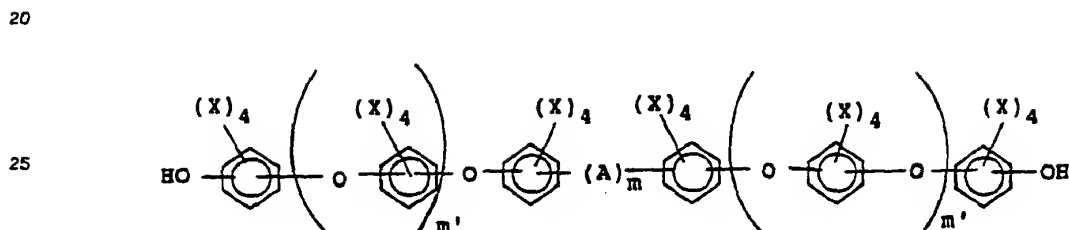
(V)



(VI)



(VII)



wherein A is a hydrocarbyl group having from 1 to 15 carbon atoms, -O-

-S-, -S-S-,



35

O

"

-S-

"

40

O

, or

O

-C-; R is hydrogen or a hydrocarbyl group having from 1 to 6 carbon atoms; each X is independently hydrogen, a hydrocarbyl or hydrocarbyloxy group having from 1 to 6 carbon atoms or a halogen atom, preferably bromine; each m independently has a value of zero to 1; and m' has a value of from zero to 50;

(b) said extender material is 4-bromomethyl-3,5-dibromo-2,6-dimethyl phenol, 2,4-bis(chloromethyl) 1,2-bis(bromomethyl)benzene, 1,3-bis(bromomethyl)-benzene, 1,4-bis(bromomethyl)benzene, 1,2-bis-(chloromethyl)benzene, 1,3-bis(chloromethyl)benzene, 1,4-bis(chloromethyl)benzene, 2,4-bis(chloromethyl)-mesitylene, 4,6-bis(chloromethyl)-m-xylene, 2,5-bis(chloromethyl)-p-xylene, and combinations thereof;

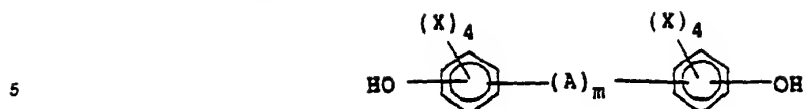
(c) said vinylbenzyl halide is vinylbenzyl chloride or vinylbenzyl bromide; and

(d) said polar aprotic solvent is dimethylformamide, dimethyl acetamide, dimethylsulfoxide, N-methyl pyrrolidinone, dioxane, acetonitrile, tetrahydrofuran, ethylene glycol dimethyl ether, 1,2-dimethoxy propane, tetramethylene sulfone, hexamethyl phosphoramide, methyl ethyl ketone, methyl isobutyl ketone, acetone or mixtures thereof.

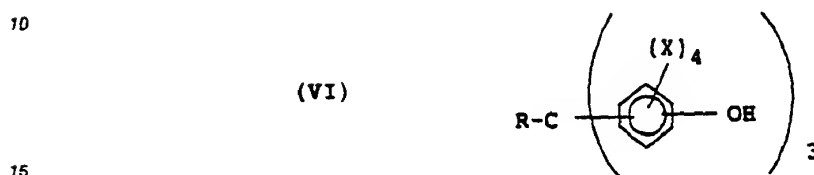
9. A method as claimed in Claim 5 or Claim 6 wherein

(a) said material containing a plurality of aromatic hydroxyl groups is a material represented by the following formulas V, VI or VII

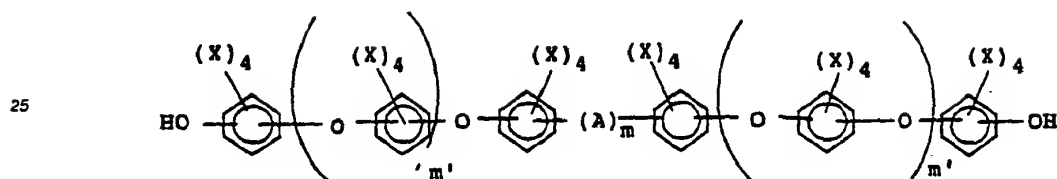
(V)



(VI)



(VII)



wherein A is a hydrocarbonyl group having from 1 to 10 carbon atoms, -O-,

30 -S-, -S-S-,



-S-

35 O

"

-S-

"

40 O

or



45 -C-; R is hydrogen or a hydrocarbonyl group having from 1 to 4 carbon atoms; each X is independently hydrogen, a hydrocarbonyl or hydrocarbonyloxy group having from 1 to 4 carbon atoms or a halogen atom, preferably bromine; each m independently has a value of zero or 1; and m' has a value of from zero to 20;

(b) said extender material is 4-bromomethyl-3,5-dibromo-2,6-dimethyl phenol, 2,4-bis(chloromethyl) 1,2-bis(bromomethyl)benzene, 1,3-bis(bromomethyl)benzene, 1,4-bis(bromomethyl)benzene, 1,2-bis(chloromethyl)benzene, 1,3-bis(chloromethyl)benzene, 1,4-bis(chloromethyl) benzene, 2,4-bis(chloromethyl)mesitylene, 4,6-bis(chloromethyl)-m-xylene, 2,5-bis(chloromethyl)-p-xylene, and combinations thereof;

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(c) said vinylbenzyl halide is vinylbenzyl chloride or vinylbenzyl bromide; and

(d) said polar aprotic solvent is dimethylformamide, dimethyl acetamide, dimethylsulfoxide, N-methyl pyrrolidinone, dioxane, acetonitrile, tetrahydrofuran, ethylene glycol dimethyl ether, 1,2-dimethoxy propane, 55 tetramethylene sulfone, hexamethyl phosphoramide, methyl ethyl ketone, methyl isobutyl ketone, acetone or mixtures thereof.

10. A method as claimed in any one of Claims 5 to 9 wherein the reaction is conducted at (1) a temperature of from -30°C to 100°C for 0.5 to 20 hours, (2) a temperature of from 0°C to 80°C for 0.5 to 15 hours, or (3) a temperature of from 15°C to 60°C for 0.5 to 6 hours.

11. A method for the preparation of cured compositions containing a plurality of vinylbenzyl ether groups which comprises a 2-step heating cycle, wherein the first step is conducted at a temperature of from 60°C to 130°C and the second step is conducted at a temperature of from 175°C to 260°C.

12. A curable composition comprising a monomer or an oligomer as claimed in any one of Claims 1 to 3.

13. A curable composition according to Claim 12 further comprising a curable resin selected from the group consisting of bismaleicimide, polycyanates of polyphenols, polypropargyl ethers of polyphenols, epoxides and mixtures thereof.

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(19)



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(12)

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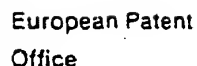
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(54) **New monomers and oligomers containing a plurality of vinylbenzyl ether groups, method for their preparation and cured products therefrom.**

(57) Monomers and oligomers containing a plurality of vinylbenzyl ether groups are prepared by reacting a material containing a plurality of aromatic hydroxyl groups such as tetramethyltetrabromobisphenol A with a vinylbenzyl halide such as vinylbenzyl chloride in the presence of a polar aprotic solvent such as dimethylformamide. The monomers and oligomers prepared by this process have an improvement in one or more properties selected from dielectric constant (before and/or after moisture absorption) or thermal stability. Also disclosed are new monomers and oligomers containing a plurality of vinylbenzyl ether groups such as bis(vinylbenzyl)-ether of dicyclopentadienyl bisdimethylphenol.

EP 0 260 443 A3



Application number
EP 87 11 1783

DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)		
X	EP - A - 0 106 023 (UNION CARBIDE) * Page 35; page 63, lines 22-35; examples 2,5 *	5,10	C 07 C 43/215 C 07 C 43/225 C 07 C 41/16 C 08 G 65/48 C 08 F 12/34 C 08 L 71/00		
A,D	-- US - A - 4 116 936 (E.C. STEINER) * Whole document *	1-4, 12,13			
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)		
			C 07 C 41/00 C 07 C 43/00 C 08 G 65/00		
XXXXXXXXXXXXXXXXXXXXXXXXXXXXX					
Place of search		Date of completion of the search	Examiner		
THE HAGUE		09-12-1987	WRIGHT		
CATEGORY OF CITED DOCUMENTS			T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document		
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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claims:
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

X LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims 1-10,12,13
2. Claim 11

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☒ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims: 1-10,12,13